Supporting Information for

The Role of $AlCl_3$ in Controlling the Valency of Copper in Two New Hybrid Materials Constructed from Decavanadate and Cu(1,10-Penanthroline) Complex

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Table S1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $V_{10}O_{28}$-CuCl-phen at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
V(1)	3772(1)	9826(1)	2536(1)	1	22(1)
V(2)	4770(1)	7721(1)	3860(1)	1	19(1)
V(3)	3120(1)	10194(1)	4750(1)	1	17(1)
V(4)	7397(1)	9753(1)	2997(1)	1	22(1)
V(5)	5782(1)	12059(1)	3819(1)	1	20(1)
O(1)	7544(3)	11523(3)	3241(2)	1	24(1)
O(2)	5748(3)	9727(3)	2062(2)	1	24(1)
O(3)	6226(4)	13609(3)	3849(3)	1	32(1)
O(4)	1709(3)	10308(3)	5594(2)	1	23(1)
O(5)	3037(3)	8239(3)	4834(2)	1	19(1)
O(6)	4407(3)	11671(3)	2819(2)	1	24(1)
O(7)	5221(3)	9904(2)	4054(2)	1	18(1)
O(8)	8919(4)	9599(4)	2370(3)	1	34(1)
O(9)	5907(3)	8060(3)	5192(2)	1	19(1)
O(10)	6573(3)	7956(3)	3236(2)	1	23(1)
O(11)	3414(3)	8092(3)	2853(2)	1	23(1)
O(12)	9770(4)	13446(3)	2726(2)	1	31(1)
O(13)	10917(4)	16059(4)	2843(3)	1	32(1)
O(14)	2637(4)	9830(4)	1563(2)	1	33(1)
O(15)	4311(4)	6173(3)	3885(2)	1	28(1)
O(16)	2196(3)	10105(3)	3636(2)	1	24(1)
O(17)	7824(4)	6177(4)	5788(3)	1	37(1)
O(18)	-78(4)	7383(4)	4445(3)	1	34(1)
N(1)	7737(4)	13819(4)	1001(2)	1	25(1)
N(2)	9262(4)	16220(4)	926(3)	1	26(1)
Cu(1)	9288(1)	14930(1)	1972(1)	1	23(1)
Cl(1)	7458(5)	15626(4)	2839(3)	1	109(2)
C(1)	8224(5)	15780(4)	156(3)	1	24(1)
C(2)	7405(4)	14497(4)	194(3)	1	24(1)
C(3)	6976(6)	12638(5)	1067(3)	1	32(1)
H(3)	7199	12180	1616	1	38
C(4)	6307(5)	13970(5)	-575(3)	1	31(1)

C(5)	5503(6)	12693(7)	-489(4)	1	40(2)
H(5)	4768	12304	-981	1	48
C(6)	10059(6)	17423(5)	922(4)	1	34(1)
H(6)	10760	17736	1453	1	41
C(7)	5836(6)	12038(6)	341(4)	1	37(1)
H(7)	5310	11204	419	1	45
C(8)	6066(6)	14755(7)	-1396(3)	1	41(2)
H(8)	5359	14411	-1916	1	49
C(9)	7969(5)	16535(5)	-661(3)	1	32(1)
C(10)	9868(8)	18227(5)	138(5)	1	42(2)
H(10)	10442	19059	152	1	51
C(11)	6847(6)	15987(7)	-1433(4)	1	40(2)
H(11)	6645	16477	-1968	1	48
C(12)	8831(7)	17784(6)	-651(4)	1	42(2)
H(12)	8703	18313	-1174	1	51

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Anisotropic displacement parameters ($Å^2x10^3$) for $V_{10}O_{28}$-CuCl-phen at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V(1)	22(1)	20(1)	23(1)	1(1)	-2(1)	3(1)
V(2)	20(1)	13(1)	25(1)	0(1)	1(1)	0(1)
V(3)	14(1)	14(1)	24(1)	1(1)	0(1)	2(1)
V(4)	20(1)	18(1)	26(1)	0(1)	4(1)	1(1)
V(5)	22(1)	13(1)	25(1)	0(1)	2(1)	4(1)
O(1)	24(2)	20(2)	28(2)	0(2)	6(1)	5(1)
O(2)	25(2)	24(2)	23(2)	-1(2)	2(1)	2(1)
O(3)	39(2)	13(2)	44(2)	-2(2)	8(2)	6(2)
O(4)	17(1)	22(2)	30(2)	2(1)	2(1)	2(1)
O(5)	18(1)	14(2)	25(2)	0(1)	1(1)	2(1)
O(6)	27(2)	20(2)	26(2)	3(2)	0(1)	6(1)
O(7)	17(1)	13(1)	22(1)	0(1)	1(1)	1(1)
O(8)	27(2)	37(2)	38(2)	2(2)	12(2)	0(2)
O(9)	19(1)	14(1)	26(2)	2(1)	1(1)	2(1)
O(10)	22(2)	16(2)	31(2)	1(1)	5(1)	1(1)
O(11)	24(2)	18(2)	25(2)	-1(1)	-2(1)	-1(1)
O(12)	27(2)	27(2)	36(2)	-3(2)	-3(2)	10(2)
O(13)	28(2)	30(2)	33(2)	-8(2)	-2(2)	-6(2)
O(14)	35(2)	34(2)	29(2)	3(2)	-8(2)	5(2)
O(15)	33(2)	13(2)	36(2)	-1(2)	2(2)	-1(2)
O(16)	20(2)	24(2)	26(2)	2(1)	-3(1)	1(2)
O(17)	27(2)	30(2)	56(2)	4(2)	-3(2)	12(2)
O(18)	24(2)	36(2)	42(2)	4(2)	1(2)	-2(2)
N(1)	26(2)	23(2)	23(2)	-1(2)	-1(2)	0(2)
N(2)	28(2)	20(2)	28(2)	1(2)	2(2)	1(2)
Cu(1)	22(1)	22(1)	23(1)	-1(1)	-1(1)	0(1)
Cl(1)	110(2)	78(2)	143(3)	19(2)	32(2)	9(2)
C(1)	26(2)	24(2)	23(2)	6(2)	3(2)	1(2)
C(2)	22(2)	27(2)	21(2)	2(2)	0(2)	-2(2)
C(3)	37(2)	26(2)	30(2)	-4(2)	0(2)	-3(2)
C(4)	28(2)	41(2)	24(2)	6(2)	-3(2)	-4(2)
C(5)	35(2)	49(3)	33(2)	0(2)	-5(2)	-13(2)
C(6)	38(2)	21(2)	43(2)	1(2)	0(2)	3(2)

C(7)	40(2)	30(2)	38(2)	-6(2)	3(2)	-8(2)
C(8)	40(2)	62(4)	23(2)	19(3)	-7(2)	-3(2)
C(9)	33(2)	35(2)	30(2)	14(2)	5(2)	8(2)
C(10)	53(3)	22(2)	53(3)	5(2)	6(2)	10(2)
C(11)	41(2)	56(3)	28(2)	18(2)	0(2)	10(2)
C(12)	53(3)	34(2)	44(3)	17(2)	8(2)	16(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $V_{10}O_{28}$-CuO-phen at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
V(1)	3762(2)	-171(2)	2536(2)	1	36(1)
V(2)	5234(2)	2279(2)	6136(2)	1	34(1)
V(3)	3115(2)	186(2)	4752(2)	1	32(1)
V(4)	2607(2)	250(2)	7002(2)	1	36(1)
V(5)	4222(2)	-2062(2)	6182(2)	1	35(1)
Cu(1)	713(2)	5074(2)	8031(1)	1	39(1)
O(1)	2446(8)	-1501(6)	6765(5)	1	34(2)
O(2)	4274(9)	271(7)	7925(5)	1	39(2)
O(3)	3769(9)	-3597(6)	6153(6)	1	44(2)
O(4)	1709(7)	323(6)	5581(5)	1	36(2)
O(5)	3024(7)	-1758(6)	4825(5)	1	30(2)
O(6)	5605(8)	-1674(7)	7174(5)	1	38(2)
O(7)	4785(7)	105(6)	5954(5)	1	28(2)
O(8)	1095(9)	418(7)	7616(6)	1	47(2)
O(9)	4088(8)	1952(6)	4792(5)	1	35(2)
O(10)	3429(8)	2046(7)	6765(5)	1	36(2)
O(11)	3419(8)	-1904(7)	2855(5)	1	35(2)
O(12)	220(9)	6542(7)	7263(5)	1	45(2)
O(13)	-934(9)	3917(8)	7152(6)	1	51(2)
O(14)	2634(9)	-161(7)	1577(6)	1	45(2)
O(15)	5676(9)	3812(7)	6111(6)	1	44(2)
O(16)	2178(8)	118(6)	3628(5)	1	37(2)
O(17)	-2166(9)	6188(7)	5790(6)	1	53(2)
O(18)	78(10)	2613(8)	5553(6)	1	57(2)
O(19)	2519(9)	4382(7)	7179(6)	1	49(2)
N(1)	2268(10)	6188(8)	8989(6)	1	37(2)
N(2)	737(10)	3778(9)	9058(7)	1	41(2)
C(1)	1759(13)	4207(11)	9858(8)	1	42(3)
C(2)	2616(12)	5511(11)	9804(8)	1	37(3)
C(3)	3022(14)	7379(12)	8941(9)	1	47(3)
H(1)	2781	7852	8402	1	56
C(4)	3702(13)	6046(11)	10562(8)	1	41(3)
C(5)	4490(15)	7311(13)	10497(10)	1	54(3)
H(2)	5205	7696	11001	1	65

C(6)	-51(15)	2594(11)	9084(10)	1	51(3)
H(3)	-776	2291	8562	1	61
C(7)	4183(15)	7981(13)	9668(10)	1	58(4)
H(4)	4726	8810	9588	1	69
C(8)	3922(16)	5238(14)	11377(9)	1	58(4)
H(5)	4645	5581	11890	1	69
C(9)	2058(14)	3475(11)	10654(9)	1	45(3)
C(10)	142(16)	1768(12)	9851(10)	1	57(3)
H(6)	-428	933	9835	1	69
C(11)	3170(15)	4040(14)	11450(9)	1	55(3)
H(7)	3353	3572	12002	1	66
C(12)	1191(16)	2219(12)	10629(11)	1	61(4)
H(8)	1329	1685	11149	1	74

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Anisotropic displacement parameters ($Å^2x10^3$) for $V_{10}O_{28}$-CuO-phen at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V(1)	38(1)	29(1)	40(2)	1(1)	-3(1)	0(1)
V(2)	34(1)	22(1)	43(2)	1(1)	0(1)	-6(1)
V(3)	28(1)	23(1)	43(2)	1(1)	-3(1)	-1(1)
V(4)	34(1)	28(1)	46(2)	1(1)	2(1)	-2(1)
V(5)	37(1)	22(1)	45(2)	-1(1)	1(1)	1(1)
Cu(1)	39(1)	32(1)	43(1)	-2(1)	-5(1)	-4(1)
O(1)	34(4)	24(4)	40(4)	-5(3)	-1(3)	-2(3)
O(2)	44(4)	33(4)	37(4)	2(3)	-8(3)	-2(3)
O(3)	55(5)	23(4)	52(5)	-5(3)	-2(4)	4(4)
O(4)	27(4)	29(4)	51(5)	3(3)	3(3)	-7(3)
O(5)	28(3)	22(4)	41(4)	1(3)	0(3)	-2(3)
O(6)	33(4)	32(4)	45(5)	2(3)	-12(3)	-1(3)
O(7)	31(3)	15(3)	38(4)	4(3)	-2(3)	4(3)
O(8)	45(4)	36(5)	58(5)	-1(3)	6(4)	-8(4)
O(9)	30(4)	31(4)	44(4)	8(3)	-2(3)	-4(3)
O(10)	31(4)	29(4)	45(4)	0(3)	-5(3)	-9(3)
O(11)	35(4)	31(4)	38(4)	3(3)	-2(3)	-4(3)
O(12)	54(5)	31(4)	45(5)	-4(3)	-7(4)	3(3)
O(13)	47(5)	47(5)	55(5)	-4(4)	-15(4)	-4(4)
O(14)	51(4)	30(4)	53(5)	2(3)	-7(4)	7(4)
O(15)	50(4)	28(4)	52(5)	4(3)	-13(4)	-11(3)
O(16)	36(4)	29(4)	46(4)	1(3)	-3(3)	5(3)
O(17)	43(4)	37(5)	75(6)	-6(4)	-11(4)	7(4)
O(18)	47(5)	49(5)	71(6)	-3(4)	-3(4)	-8(4)
O(19)	48(5)	33(4)	64(6)	-5(3)	15(4)	2(4)
N(1)	40(5)	27(5)	41(5)	-5(4)	-2(4)	-6(4)
N(2)	40(5)	37(6)	46(6)	2(4)	-5(4)	-6(4)
C(1)	37(6)	49(7)	41(7)	16(5)	1(5)	-12(6)
C(2)	38(6)	43(7)	31(6)	6(5)	2(5)	-6(5)
C(3)	50(7)	42(7)	49(7)	6(6)	4(6)	-4(6)
C(4)	38(6)	45(7)	40(7)	5(5)	-8(5)	-7(6)
C(5)	47(7)	60(9)	51(8)	1(6)	-8(6)	-13(7)
C(6)	61(8)	27(6)	62(8)	0(6)	0(6)	-10(6)
C(7)	50(7)	47(8)	71(9)	0(6)	4(7)	-23(7)

C(8)	51(8)	77(10)	40(8)	-4(7)	-6(6)	-5(7)
C(9)	50(7)	37(7)	49(7)	15(5)	4(6)	2(6)
C(10)	65(8)	37(7)	70(9)	5(6)	8(7)	2(7)
C(11)	50(7)	80(10)	38(7)	23(7)	-4(6)	-2(7)
C(12)	68(9)	41(8)	79(10)	18(7)	6(8)	15(7)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S5: The selected bond lengths in the hybrid materials $V_{10}O_{28}$-CuCl-phen and $V_{10}O_{28}$-CuO-phen

Bond	Bond length
$V^{+5}-O_v$	1.55 −1.65 Å
$V^{+5}-O_e$	1.74 −1.85 Å
$V^{+5}-O_t$	2.00−2.40 Å
$V^{+4}-O_e$	1.66 −1.9 Å
$V^{+4}-O_t$	2.00− 2.01 Å

Table S6: The bond lengths and the protonation sites fixed by the power function of the V-O bonds in the $[V_{10}O_{28}]^{6-}$ unit of the hybrids.

Atoms	Bond length, R (Å)	S=(R/1.791)^(-5.1)	ΣS
O_7—V_2	2.2547(1)	0.30	1.98
O_7—V_3'	2.1101(1)	0.43	
O_7—V_3	2.0827(1)	0.46	
O_7—V_5	2.2711(1)	0.29	
O_7—V_4	2.3890(1)	0.23	
O_7—V_1	2.3450(1)	0.25	
O_5—V_5	2.1035(1)	0.44	1.39
O_5—V_3	2.0349(1)	0.52	
O_5—V_2	2.1144(1)	0.42	
O_9—V_2	2.0094(1)	0.55	1.92
O_9—V_3	1.8814(1)	0.77	
O_9—V_5	1.9834(1)	0.59	
O_{15}—V_2	1.6115(1)	1.71	
O_3—V_5	1.6065(1)	1.74	
O_{14}—V_1	1.6053(1)	1.74	
O_8—V_4	1.5894(0)	1.83	
O_1—V_5	1.8562(1)	0.83	1.70
O_1—V_4	1.8418(1)	0.86	
O_6—V_1	1.9344(1)	0.67	1.82
O_6—V_5	1.7408(1)	1.15	
O_2—V_4	1.8387(1)	0.87	1.81
O_2—V_1	1.8125(1)	0.94	
O_{11}—V_1	1.8583(1)	0.82	1.72
O_{11}—V_2	1.8283(1)	0.90	
O_{10}—V_4	1.9488(1)	0.65	1.75
O_{10}—V_2	1.7578(1)	1.10	
O_4—V_3	1.6940(1)	1.32	1.84
O_4—V_4	2.0372(1)	0.51	
O_{16}—V_1	2.0694(1)	0.47	1.91
O_{16}—V_3	1.6686(1)	1.43	

Table S7: Important bond distances of the bonds involved in supramolecular interactions to form three dimensional network.

No.	Atom 1	Atom 2	Type of bond	Bond Distance (Å)	Comments
1	Cu	Cl	Covalent	2.1661	Cl forms H bond with C-H
2	Cu	$O_{(H2O)}$ (1)	Covalent	1.9761	
3	Cu	$O_{(H2O)}$ (2)	Covalent	1.991	
4	$O_{(H2O)}$ (Attached to Cl)	O(attached to V in POM)	No bond	2.6662	The H attached to the O attached to Cl forms H-bond with O attached to V. Here the H to O has not been fixed.
5	H attached to C of phen	O(attached to V in POM)	H-bond	2.3613	Have role in the formation of supramolecular assembly
6	Cl attached to Cu	H attached to C of phen	H-bonding	2.6314	Have role in the formation of supramolecular assembly
7	C of one phen unit	C of next phen unit	π-π stacking	3.95*	Have role in the formation of supramolecular assembly

*Average bond distance

Figures

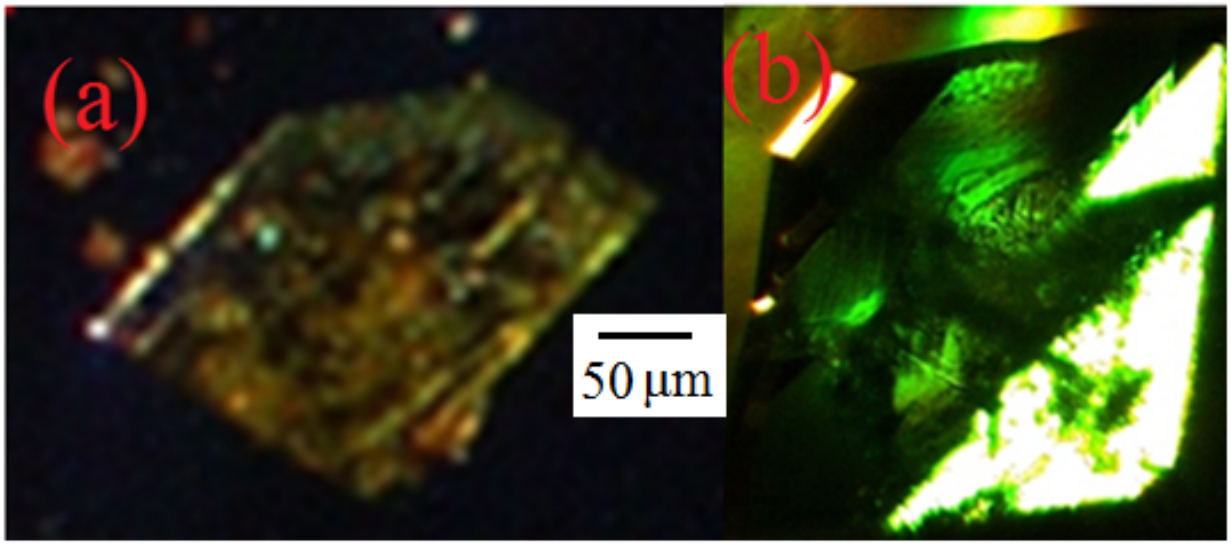

Figure S1: (a) The optical image of $V_{10}O_{28}$-CuO-phen and (b) $V_{10}O_{28}$-CuCl-phen

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